

## **RARE EARTH DOPED LUMINESCENT GLASS AND COLD LIGHT SOURCE DEVICE**

### **FIELD OF THE INVENTION**

[0001] The invention relates to rare earth doped luminescent glasses and methods of generating white light in a system using such luminescent glasses in combination with cold light sources such as light emitting diodes (LEDs) emitting blue and/or UV light or such as gas discharge lamps.

### **BACKGROUND OF THE INVENTION**

[0002] In the lighting industry there is a continuous demand for the increase in power efficiency. Therefore, prior art incandescent light sources are being more and more replaced by more power efficient light sources such as LEDs and gas discharge lamps.

[0003] In particular, LEDs are becoming increasingly popular as light sources for lighting applications ranging from interior illumination, appliance indicators, displays, to outdoor high intensity lighting such as needed in automotive, aerospace, and recreational facilities. A limitation of com-

mercial LEDs is that they produce light of limited spectral range (e.g. red, green or blue), and for many applications it is both desirable and necessary that the illumination source produce instead white light with a blackbody temperature between 2700 K and 3000K and a high color rendering index.

[0004] White light LEDs can be prepared in a number of ways. One way is to combine two monochromatic colors (for example blue and yellow) called complementary colors. Two such complementary colors at the appropriate ratio of intensities will be perceived as white light by the human eye. In the case of a white LED, this is achieved by using a blue LED in combination with a phosphor material that converts a portion of the blue LED light into yellow fluorescence. The resultant blue/yellow emission is perceived as white to the eye. The typical phosphor for this application is yttrium aluminum garnet (YAG) crystals doped with cerium (see for example "The Blue Laser Diode", S. Nakamura and G. Fasol, Springer, 1997). Such sources lack red and green components giving poor color rendering properties.

[0005] Other phosphor materials include organic dyes and semiconductor nano particles. These have the advantage that they provide an opportunity to combine multiple colors to create white emission. However, all of these phosphor materials must be placed in a suitable encapsulate, including the cerium doped YAG. Commonly this is an organic plastic, with limited temperature stability and little resistance to chemical and mechanical degradation when exposed for extended periods of time to UV and blue light.

[0006] Alternatively, the possibility exists to dope glass with rare earth cations to produce white fluorescence. A number of rare earth doped glass formulations are known, with particular applicability as ophthalmic, filter, laser, upconversion and phosphors. However none of the prior art discusses use of these rare earth formulations for creating white light of sufficiently high quality to function in indoor illumination applications. For example, JP 2000159543 discloses a silicate glass ceramic containing rare earth cations for producing desirable long lasting luminescence. JP 2000281382 discloses silicate glasses and glass ceramics containing rare earth cations for producing desirable long lasting luminescence. EP 0 847 964 A1 and JP 8133780 A disclose silicate glasses containing europium or terbium, while EP 0 709 345 A1 and JP 9202642 A disclose fluorophosphate compositions containing either europium or terbium to produce fluorescent glasses of specific colors. EP 0 775 673 A1 and JP 10167755 A disclose fluorophosphate glass compositions containing europium in the divalent state, or terbium along with either samarium or manganese, to produce glasses that give blue or white fluorescence, respectively, when excited in the UV part of the spectrum to be used as an indicator card for identification of the location of UV laser beams.

[0007] From US 2003/0025449 A1 a hybrid LED is known that comprises a radiation-emitting semiconductor body which is surrounded by a housing which comprises a glass body made of a luminescent glass for converting the UV radiation into visible light. However, any specific composition for the luminescent glass is not disclosed. A similar LED is known from JP 2002246651 A.

[0008] Further reference is made to JP 2001214162 A which discloses a phosphor comprising oxynitride glass as a matrix material. The glass comprises 20 to 50 mol-% of  $\text{CaCO}_3$ , up to 30 mol-% of  $\text{Al}_2\text{O}_3$ , 25 to 60 mol-% of  $\text{SiO}_2$ , 5 to 50 mol-% of  $\text{AlN}$  and 0.1 to 20 mol-% of rare earth or transition metals.

#### SUMMARY OF THE INVENTION

[0009] The current invention relates to the use of particular types of rare earth containing glasses in combination with cold light sources that emit colored light, such as UV/blue LEDs, to generate light of different wavelengths, in particular to generate white light.

[0010] Accordingly, it is a first object of the invention is to disclose improved luminescent glasses that are highly effective in the conversion of light.

[0011] It is a second object of the invention to disclose a cold white light source employing a rare earth doped luminescent glass as a wavelength conversion material.

[0012] It is a third object of the invention is to provide improved white LED or gas-discharge systems that employ a luminescent glass, that may contain high concentrations of multiple rare earth ions and possess other properties such as physical and thermal properties that are compatible with conventional melting, forming and manufacturing procedures.

[0013] A further object of the invention is to provide improved white LED or other cold light systems in which a doped

rare earth containing luminescent glass, in particular a phosphor glass, in the form of rod, disk, powder or film structure is placed adjacent to one or more UV or blue LED or other cold light source and functions as a wavelength conversion material to produce white light.

[0014] These and other objects are achieved according to the invention by a luminescent glass comprising a base glass doped with 0.001 to 30 wt.-% of rare earth oxides on an oxide basis, said base glass comprising 1 wt.-% of water at the most and 1 wt.-% of  $B_2O_3$  at the most. Preferably, the glass does not contain any water at all (0.1 wt.-% or 0.01 wt.-% at the most). Also preferably, the glass does not contain any  $B_2O_3$  (0.1 wt.-% or 0.01 wt.-% at the most).

[0015] Such glasses facilitate an optimization of the glasses with respect to a high UV-transmissivity and to a low maximum phonon energy. Thus the losses of the luminescent glass body are kept as small as possible.

[0016] The glasses may be optimized with respect to their maximum phonon energy which should be kept as small as possible thus reducing losses. In case excitation of the luminescent glass is performed in the UV-region then the luminescent glass can also be optimized with respect to a high UV-transmissivity.

[0017] Preferably, the luminescent glass is used as a solid glass body this leading to a good optical homogeneity, to a high mechanical, thermal, and chemical resistance as well as

to a long-term stability of the absorption and emission characteristics.

[0018] The cold light source may be an LED or any other cold light source, such as a gas-discharge lamp, a neon lamp, etc.

[0019] In case LEDs are used, then preferably LEDs emitting in the blue and UV-region are used in combination with the luminescent glass according to the invention to produce high-power white LED sources.

[0020] The rare earth doping used to obtain the luminescent characteristic of the glass is preferably as high as possible to obtain a highly effective conversion and a bright light source.

[0021] Herein, the local coordination numbers of the rare earth ions and the crystal field can be tailored by means of the glass composition to yield the desired color emission. The broad adsorption of the rear earth ions during the transitions  $4f \rightarrow 5d$  (e.g.  $\text{Eu}^{2+}$ :  $4f^6 5d^1 \rightarrow 4f^7$  or at Ce) is used to absorb the light of a semiconductor emitter emitting a short wavelengths spectrum. The emission is then performed in a spectral range shifted more to longer wavelengths.

[0022] The absorption and emission characteristics of the glass body are primarily influenced by the amount of doping with rear earth ions. The optical transitions of 4f electron systems of Europium can be influenced by the glass composition only to a limited extent. However, the base glass can be opti-

mized with respect to its optical characteristics independently from the doping with rear earth ions to yield in particular a high quantum efficiency of the electron transitions ("low phonon energy glass") and to yield a high UV-transmissivity when light sources emitting in the UV-region are used, and to tailor the glass to emit at a particular color temperature range.

[0023] Therefore, a wide variety of base glasses may be used for doping with rear earth ions, if they are particularly selected to have a maximum phonon energy as small as possible and to have a UV-transmissivity as high as possible.

[0024] Principally, all glasses based on the classical glass formers  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ , and  $\text{P}_2\text{O}_5$  or  $\text{GeO}_2$  are suitable. A wide variety of these glasses is known for technical and optical applications. These glasses include lead-silicate glasses (flint glasses), soda-lime glasses (crown glasses), alkali-alkaline-earth silicate glasses, lanthanum oxide borate glasses, barium oxide silicate glasses, chalcogenide glasses and halaid glasses.

[0025] Such "technical" or "optical" glasses may be tailored with respect to their characteristics by adding other oxides.

[0026] To reduce the maximum phonon energies, in particular the content of  $\text{B}_2\text{O}_3$  is kept as small as possible.

[0027] Even when the maximum phonon energy is adjusted in an optimal way, excited rear earth ions may relax undesirably without emission, in particular with  $\text{OH}^-$ -groups present in

the glass. Therefore, according to the invention it is desired, to make the glass extremely low on  $\text{OH}^-$  which can be obtained by "dry" melting, e.g. by adding halogenides such as  $\text{Cl}^-$ , or by blowing dry oxygen or halogenide gas into the melt. In this way a quantum efficiency of the phonon transitions of  $> 80 \%$ , preferably  $> 90 \%$  can be reached so that a maximum of  $20 \%$  (preferably only  $10 \%$  of the excited levels of the non-emitting processes) are relaxed ("low phonon energy glass").

[0028] Also by the addition of oxides of heavy metals or transition metals, in particular Bi, Te, Sb, Ge, Gd, Ga, Pb, V, Nb, the phonon energy will be reduced. The transition metals are highly polarizable and thereby facilitate to broaden the optical transitions (by means of Stark splitting). Such glasses having additions of  $\text{Bi}_2\text{O}_3$  which are preferably in the range between 10 and 85 mol-% are able to reduce the maximum phonon energies to less than  $1000 \text{ cm}^{-1}$  (cf. JP-H3-295828 with respect to upconversion lasers).

[0029] To this end, glasses comprising at least 10 mol-% of  $\text{Bi}_2\text{O}_3$  and at least 10 mol-%  $\text{Si}_2\text{O}$  can be used that may also comprise at least 20 mol-%  $\text{TeO}_2$ , at least 1 mol-%  $\text{R}_2\text{O}$  and at least 1 mol-%  $\text{ZnO}$  (e.g. 75 mol-%  $\text{TeO}_2$ , 5 mol-%  $\text{Na}_2\text{O}$ , 20 mol-%  $\text{ZnO}$ ).

[0030] With these glasses an optimum between a low phonon energy, broad emission, and high UV-transmissivity can be found.



[0031] Also by applying chalcogenide glasses or halogenide glasses instead of oxide glasses the phonon energies may be reduced.

[0032] An example for such a base glass is 53 ZrF<sub>3</sub>, 20 BaF<sub>2</sub>, 3 LaF<sub>3</sub>, 3 AlF<sub>3</sub>, 20 NaF, 1 ErF<sub>3</sub> (ZBLAN).

[0033] Particularly low phonon energies and very positive UV-transmissivities can be reached with glasses of the fluorophosphate type. E.g. a base glass having the following composition may be used:

P <sub>2</sub> O <sub>5</sub>	> 7
MgO + CaO + SrO	> 1
Al <sub>2</sub> O <sub>3</sub>	> 5
BaO	> 5
R <sub>2</sub> O	> 0.1
F/F <sub>2</sub>	> 10
SiO <sub>2</sub>	≥ 0
other oxides	up to 20.

[0034] Herein the phonon energies are at 1100 cm<sup>-1</sup> maximum and the UV-edge is below 250 nm.

[0035] According to a further development of the invention, the luminescent glass is an at least partially segregated glass comprising at least a certain fraction of the rare earth ions within the segregated regions.

[0036] According to a further embodiment of the invention, the rear earth ions may at least partially be included in crystallite inclusions of the glass.

[0037] By these measures, the crystal field and the coordination numbers of the rear earth ions may be tailored in a particular way to match the emission characteristics of the luminescent glass in a broad range to a particular application.

[0038] Glasses particularly suited for converting LED light of the blue or UV spectrum (or light of other cold light sources emitting colored light) into white light are highly doped rare earth containing phosphate phosphor glasses.

[0039] The invention involves the recognition that certain combinations and dopant levels of rare earth cations, and high total levels of rare earth content, higher than those normally expected to produce bright fluorescence, are desirable in certain white cold light source system designs. Such total rare earth content levels were thought to be previously prohibitive, either because of manufacturing difficulties associated with solubility issues of rare earth materials in glass or because of decreased fluorescence performance, due to issues of either self quenching or quenching of the rare earth excited states by energy transfer to phonon (vibrational) modes within the host glass involved in the fluorescence transitions producing white light, when rare earth concentration levels achieve a critical value. The latter phenomena is referred to as concentration quenching. See, e.g. US patent 4,239,645 which discloses that high total neodymium (Nd) oxide contents cause difficulties in oscillating and amplifying a laser glass due to

self quenching of Nd excited states by energy transfer between Nd cations and phonon modes within a phosphate host glass.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0040] Upon further study of the specification in conjunction with the drawings further objects and advantages of this invention will become apparent to those skilled in the art.

[0041] Figure 1 shows the absorption spectrum of highly doped phosphate phosphor glasses of the present invention.

[0042] Figures 2 through 4 show the emission spectra of highly doped phosphate phosphor glass examples of the present invention when excited at 370nm, 380nm and 410nm, respectively.

[0043] Figure 5 is a representative image of the chromaticity diagram.

[0044] Figures 6 through 8 show the chromaticity points for fluorescence from highly doped phosphate phosphor glass examples when excited at 370nm, 380nm and 410nm, respectively.

[0045] Figures 9 and Figure 10 show a schematic representation of white LED systems prepared with a doped luminescent glass of the present invention.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0046] Apart from the wide variety of glasses discussed before, particularly phosphate phosphor glasses are disclosed by the current invention for making highly efficient luminescent glasses that are highly doped with rear earth oxides. These glasses will be described in the following.

[0047] Phosphor glasses of the present invention comprise  $P_2O_5$ ,  $Al_2O_3$ , alkali earth oxides, and alkaline earth oxides. Preferably, the glass contains a maximum of 4 weight percent, especially a maximum of 2 weight percent, of conventional additives or impurities, such as refining agents (e.g.,  $As_2O_3$ ,  $Sb_2O_3$ ), antisolarants (e.g.,  $TiO_2$ ,  $Sb_2O_3$ ,  $Nb_2O_5$ ) and  $SiO_2$  and  $ZrO_2$  which can enter the glass through dissolution of the melting vessel. The inventive glasses are doped with trivalent lanthanide oxides (oxides of elements 57-71) or trivalent rare earth oxides (lanthanide oxides and oxides of Sc and Y) in an amount exceeding 2 mol %, preferably exceeding 3 mol % and particularly preferably exceeding 4 mol%. Exemplary trivalent lanthanide/rare earth oxides are  $Y_2O_3$ ,  $Sc_2O_3$ ,  $La_2O_3$ ,  $Ce_2O_3$ ,  $Pr_2O_3$ ,  $Nd_2O_3$ ,  $Sm_2O_3$ ,  $Eu_2O_3$ ,  $Gd_2O_3$ ,  $Tb_2O_3$ ,  $Dy_2O_3$ ,  $Ho_2O_3$ ,  $Er_2O_3$ ,  $Tm_2O_3$ , and  $Yb_2O_3$ . The phosphor glasses according to the invention are highly doped with preferably trivalent terbium, europium, and cerium and/or thulium. In these glasses, the oxygen in the metal oxides can optionally be replaced by fluorine up to 90%, or other halogens and anions such as nitrogen and carbon up to 10%.

[0048] In general, the glasses have a  $P_2O_5$  content of 50 to 75 mol %, for example, 51, 52, 53, 54, 55, 56, 57, 58,

59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74 mol %. Further preference is given to glasses having a  $P_2O_5$  content above 60 mol %, more preferably above 65 mol %, even more preferably above 70 mol %. It is believed that higher levels of  $P_2O_5$  enhance the solubility for rare earth ions and reduce harmful quenching of the rare earth excited states involved in the transitions generating fluorescence.

[0049] In addition, in general, the glasses have a  $Al_2O_3$  content of 3 to 15 mol %, for example, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 mol %. Preference is given to glasses having an  $Al_2O_3$  content above 5 mol %, more preferably above 8 mol %, and even more preferably over 10 mol % since these glasses are characterized by improved chemical durability.

[0050] The alkali metal oxides used in the inventive glasses are  $Na_2O$ ,  $K_2O$ ,  $Li_2O$ ,  $Rb_2O$  and  $Cs_2O$ , preferably  $Na_2O$ ,  $Li_2O$ ,  $K_2O$  and  $Cs_2O$ , and especially  $Li_2O$ ,  $K_2O$  and  $Na_2O$ . The amount of combined alkali metal oxides is, for example, 0 to 35 mol %, for example, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34 mol %, preferably 5 to 30 mol %. These additives enhance meltability of the compositions of this invention.

[0051] The alkaline metal oxide used in the inventive glasses are  $MgO$ ,  $CaO$ ,  $SrO$  and  $BaO$ . However,  $ZnO$  can be used interchangeably for these alkaline metal oxides. Preferably  $MgO$ ,  $BaO$  and  $ZnO$  are the employed metal oxides at levels of, for example, 0 to 35 mol %, for example, 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 12, 13, 14, 15, 16, 17, 18, 19, 20,

21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34 mol %, more preferably 0 to 30 mol %. These additives enhance the chemical durability of the glasses of this invention.

[0052] In accordance with one embodiment, the glasses contain trivalent  $\text{La}_2\text{O}_3$ ,  $\text{Tb}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{Ce}_2\text{O}_3$  in an amount of more than 2 mol %, for example, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0 mol %, etc., preferably more than 3 mol % and even more preferably over 4 mol %. In accordance with another embodiment, the glasses contain trivalent  $\text{La}_2\text{O}_3$ ,  $\text{Tb}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{Ce}_2\text{O}_3$  and/or  $\text{Tm}_2\text{O}_3$  in an amount of more than 2 mol %, for example, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0 mol %, etc., preferably more than 3 mol % and even more preferably over 4 mol %.

[0053] Phosphor glasses of the present invention can also contain refining agents, such as  $\text{As}_2\text{O}_3$ , and  $\text{Sb}_2\text{O}_3$ , and standard antisolarant additives, such as  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$  (as well as others, e.g.  $\text{SiO}_2$ ,  $\text{Sb}_2\text{O}_3$  and divalent cerium,  $\text{CeO}_2$ ) that prevent the glasses of this invention from exhibiting discoloration when excited by high levels of UV and blue radiation from excitation LED; as well as small levels of additional components, such as  $\text{SiO}_2$ ,  $\text{PtO}_2$ , and  $\text{ZrO}_2$ , that are present in the glass from dissolution of the melting equipment used to manufacture the glass. The combined levels of these other additives normally do not exceed 4 percent on a weight basis.

[0054] Glasses of this invention can be conventionally prepared by mixing appropriate amounts of each constituent in a batch which is then charged into a fused silica crucible and melted by induction heating, e.g., 1000 °C to as much as

1500 °C depending on the chosen composition and constituents. The glasses can then be refined at temperatures exceeding, e.g. 1200 °C from typically 2 to 4 hours, again depending on composition and thus melt viscosity, with equal intervals of oxygen and/or nitrogen gas bubbling and stirring. The glasses are then typically cast into steel molds and annealed at the transformation temperature plus about 20 °C for about 2 hours, followed by cooling to room temperature at 30 °C per hour. These procedures were followed in the examples below.

[0055] Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

[0056] In the foregoing and in the following examples, all temperatures are set forth uncorrected in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated. Examples of the highly doped rare earth containing phosphate phosphor glass of the present invention are disclosed in Table 1.

**Table 1:** Examples of highly doped rare earth containing phosphate phosphor glasses, glass compositions are expressed on a mol percent oxide basis.

Oxide	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
P <sub>2</sub> O <sub>5</sub>	67.95	68.04	68.08	68.16	68.08	67.83	67.23
Al <sub>2</sub> O <sub>3</sub>	8.45	8.46	8.46	8.47	8.46	8.43	8.36
Na <sub>2</sub> O							
K <sub>2</sub> O	9.26	9.27	9.27	9.29	9.27	9.24	9.16
BaO							
CaO							
La <sub>2</sub> O <sub>3</sub>	7.89	9.16	10.19	10.32	10.19	7.42	8.98
Ce <sub>2</sub> O <sub>3</sub>	3.71	1.24	1.24	1.24	1.24	1.24	
Tb <sub>2</sub> O <sub>3</sub>	2.62	2.63	2.63	1.32	2.63	2.63	
Eu <sub>2</sub> O <sub>3</sub>	0.12	1.21	0.13	1.21	1.21	1.21	
Pr <sub>2</sub> O <sub>3</sub>							2.47
Dy <sub>2</sub> O <sub>3</sub>							3.81
Tm <sub>2</sub> O <sub>3</sub>						2.03	
Bubbling Gas	Oxygen	Oxygen	Oxygen	Oxygen	Nitrogen	Oxygen	Oxygen

Oxide	Example 8	Example 9	Example 10	Example 11	Example 12
P <sub>2</sub> O <sub>5</sub>	68.02	68.03	66.22	68.03	70.31
Al <sub>2</sub> O <sub>3</sub>	8.45	8.45	6.97	7.17	8.74
Na <sub>2</sub> O					6.30
K <sub>2</sub> O	9.27	9.27	5.67	5.83	
BaO			7.34	3.23	
CaO				1.58	
La <sub>2</sub> O <sub>3</sub>	9.73	9.85	9.91	10.18	



Ce <sub>2</sub> O <sub>3</sub>	0.13		0.12	0.13	0.13
Tb <sub>2</sub> O <sub>3</sub>	2.63	2.63	2.56	2.63	2.72
Eu <sub>2</sub> O <sub>3</sub>	1.24	1.24	1.20	1.24	1.28
Pr <sub>2</sub> O <sub>3</sub>					
Dy <sub>2</sub> O <sub>3</sub>					
Tm <sub>2</sub> O <sub>3</sub>	0.54	0.54			
Bubbling Gas	Oxygen	Oxygen	Oxygen	Oxygen	Oxygen

[0057] The absorption spectra as recorded with a Perkin Elmer Lambda 900 spectrophotometer of the example phosphate phosphor glasses in Examples 1 through 7 (hereafter referred to as "LED-1" through "LED-7", respectively) pictured in Figure 1 provide guidance in regards to the appropriate means by which to energize, or pump, the phosphor glasses with blue or UV emitting LED. When pumped in this way, rare earth cations in the glass are electronically excited and can emit light of various colors depending on the identity of the rare earth. For the case of europium and terbium, this emission is in the red and blue/green part of the visible spectrum, respectively. For the case of cerium and thulium, this emission is in the blue part of the spectrum. For the case of praseodymium and dysprosium, multiple colors are emitted simultaneously. Figures 2 through 4 depict the emission fluorescence for the example glasses when pumped in this way at 370nm, 380nm and 410nm center wavelengths with 30nm bandwidth (FWHM) respectively.

[0058] A qualitative measure of the color of emission as perceived by the human eye is prepared by calculating the quantities (see for example the standard "Method of Measuring and Specifying Colour Rendering Properties of Light Sources",

CIE 13.3-1995, published by the Commission Internationale de l'Éclairage, ISBN 3 900 734 57 7):

$$X = \int x(\lambda)P(\lambda)d\lambda$$

$$Y = \int y(\lambda)P(\lambda)d\lambda$$

$$Z = \int z(\lambda)P(\lambda)d\lambda$$

where  $x(\lambda)$ ,  $y(\lambda)$  and  $z(\lambda)$  are the color matching functions that define the response of the red, green and blue cones within the human eye, respectively,  $P(\lambda)$  is the intensity of the emission as a function of wavelength,  $\lambda$ , and  $X$ ,  $Y$ , and  $Z$  are termed the tristimulus values for the fluorescence source. The color matching functions  $x(\lambda)$ ,  $y(\lambda)$  and  $z(\lambda)$  are tabulated in, for example, "Handbook of Colorimetry", A.C. Hardy, the Massachusetts Institute of Technology, Technology Press, 1936.

[0059] The color of the fluorescence is then quantitatively defined by ratios of these tristimulus values as:

$$x = X/(X + Y + Z)$$

and

$$y = Y/(X + Y + Z)$$

where  $x$  and  $y$  are referred to as chromaticity coordinates. In this way, a perfect white color is defined by  $x = y = 1/3$ . The color of a full range of sources can then be plotted in this way on a chromaticity diagram, see Figure 5.

[0060] However, it is generally regarded in the lighting industry that a range of colors are perceived by the eye as "white" sources. In particular, a object heated to temperatures between about 2700 K and 7000 K (referred to as a black-body radiator) emits light perceived as attractive for indoor

lighting applications. The spectral distribution of intensity with wavelength,  $\lambda$ , as a function of object temperature,  $T$ , was first derived by Plank in 1900 (see M. Plank, Verhand. der Deutschen Phys. Gesellschaft, Vol 2, pg 237, 1900) and is given by

$$I(\lambda) = 2hc^2 / \{\lambda^5 [\exp(hc/\lambda kT) - 1]\}$$

where  $h$  and  $k$  are Plank's constant ( $6.626 \times 10^{-34}$  J·s) and Boltzman's constant ( $1.381 \times 10^{-7}$  J/K), respectively, and  $c$  is the speed of light ( $2.998 \times 10^8$  m/s).

[0061] The corresponding chromaticity coordinates for the Plankian curve corresponding to a blackbody radiator at various temperatures is tabulated in, for example, "Color Science", G. Wyszecki and W.S, Stiles, John Wiley and Sons, 1967; and the representative  $x$  and  $y$  values that can be plotted on the chromaticity diagram for temperatures between 2700K and 7000K are listed in Table 2.

[0062] For this reason, chromaticity coordinates of  $x = y = 1/3$  are not alone desirable, but rather a range of  $x$  and  $y$  falling on or near a Plankian curve. A white light source can thus be defined not by chromaticity coordinates  $x$  and  $y$  alone, but should also be characterized by a color temperature (CT) of the source in degrees Kelvin.

**Table 2:** Chromaticity Diagram Coordinates for the Planckian curve between 2700K and 7000K

White Blackbody Source Temperatures (2700 to 7000K)		
T [K]	x	y
2700	0.4597	0.4106
2800	0.4517	0.4086
2900	0.4441	0.4064
3000	0.4368	0.4041
3100	0.4299	0.4015
3200	0.4233	0.3989
3300	0.4170	0.3962
3400	0.4109	0.3935
3500	0.4052	0.3907
3600	0.3997	0.3879
3700	0.3945	0.3851
3800	0.3896	0.3822
3900	0.3848	0.3795
4000	0.3804	0.3767
4100	0.3760	0.3740
4200	0.3719	0.3713
4300	0.3680	0.3687
4400	0.3643	0.3660
4500	0.3607	0.3635
4600	0.3573	0.3610
4700	0.3540	0.3586
4800	0.3509	0.3562
4900	0.3479	0.3539
5000	0.3450	0.3516
5200	0.3397	0.3472
5400	0.3347	0.3430
5600	0.3301	0.3391
5800	0.3259	0.3353
6000	0.3220	0.3318
6500	0.3135	0.3236
7000	0.3063	0.3165

[0063] The difference of chromaticity coordinates and color temperature from the Plankian curve is quantified by calculating a chromaticity difference value,  $\Delta C$ , between the chromaticity point of the fluorescence source being evaluated ( $u_s$  and  $v_s$ ) and the nearest reference point on the Plankian curve ( $u_r$  and  $v_r$ ):

$$\Delta C = [(u_s - u_r)^2 + (v_s - v_r)^2]^{1/2}$$

where the  $u$  and  $v$  coordinates are tristimulus values for the fluorescence source under evaluation and the reference source on the Plankian curve given by the standard "Method of Measuring and Specifying Colour Rendering Properties of Light Sources", CIE 13.3-1995:

$$u = 4X/(X + 15Y + 3Z)$$

and

$$v = 9Y/(X + 15Y + 3Z)$$

and a practical restriction is imposed that  $\Delta C$  be less than or equal to 0.011, preferably less than or equal to 0.005 (equal to the tolerance value for  $\Delta C$  in the standard). For reference, Figure 6 through Figure 8 show the chromaticity coordinates positions relative to the Plankian curve from 2700K to 7000K when Examples 1 through 7 are excited at 370nm, 380nm and 410nm, respectively.

[0064] It is not alone sufficient that a white source have a CT value between 2700K and 7000K and chromaticity coordinates lying near the Plankian curve between these two temperatures. It is also critical that objects of various colors be perceived by the human eye with correct color rendition. This can be achieved only when the white source has the correct balance of colors and intensities covering the entire response range of the human eye. For example, by proper selection of a

source containing proper amounts of only blue and yellow light, a source perceived to the eye as pure white can be prepared. However this source contains no green component and consequently green objects upon illuminated by this source will not be capable to reflect green light to the eye and the green color of the object will not be correctly perceived.

[0065] A quantitative value of color rendering capability of a source is given by calculating a color rendering index, CRI, given by the numerical average of eight individual special color rendering indices,  $R_1$  through  $R_8$ , as defined by the CIE standard "Method of Measuring and Specifying Colour Rendering Properties of Light Sources", CIE 13.3-1995.

$$CRI = (1/8) \sum R_i \text{ (i=1 to 8)}$$

A perfect CRI score is 100, and a functional value of CRI is more than 80. The following is a qualitative description of CRI values

CRI > 90	= close to perfect
CRI >80 to 90	= suitable for most applications
CRI of 70 to 80	= not as suitable
CRI <70	= not suitable as a lighting source

[0066] A white light source thus must satisfy three requirements, chromaticity coordinates  $x$  and  $y$  the analogous color temperature (CI) on or near the Planckian curve between 2700K and 7000K, expressed as a chromaticity difference value ( $\Delta C$ ) of less than 0.011, preferably less than 0.005, and a color rendering index (CRI) value greater than 80, preferably greater than or equal to 85.

[0067] The color chromaticity coordinates,  $x$  and  $y$ , color temperature (CI), chromaticity difference value ( $\Delta C$ ) and color rendering index (CRI) of the example glasses of the subject invention for a variety of excitation wavelengths in the UV and blue portion (between 270nm and 455nm) of the electromagnetic spectrum are given in Table 3. Emission spectra were recorded for 30nm bandwidth excitation centered on the typical LED emission wavelengths indicated in Table 3 using a Jobin Yvon Horiba SPEX FluoroLog-3 spectrofluorometer.

**Table 3:** Color Properties of example of highly doped rare earth containing phosphate phosphor glasses

Color Property	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7
For a 370nm Excitation Wavelength							
x	0.47	0.39	0.41	0.61	0.39	0.36	0.40
y	0.40	0.42	0.37	0.37	0.39	0.44	0.46
CT [K]	2411	3984	3261	1292	3917	4886	4012
$\Delta C$	0.005	0.015	0.011	0.027	0.006	0.029	0.029
CRI	82.65	83.33	86.75	51.75	87.87	71.56	-6.46
For a 380nm Excitation Wavelength							
x		0.46	0.44		0.34	0.22	0.40
y		0.41	0.40		0.41	0.22	0.46
CT [K]		2751	2937		5285	34463	4031
$\Delta C$		0.001	0.001		0.023	0.014	0.027
CRI		87.09	87.42		75.00	66.34	-9.13

For a 410nm Excitation Wavelength							
x		0.57	0.39		0.64	0.65	0.44
y		0.43	0.40		0.35	0.35	0.45
CT [K]		1781	3916		1064	1044	3306
$\Delta C$		0.007	0.007		0.001	0.0002	0.018
CRI		-14.68	86.91		24.00	23.77	12.28
For a 440nm Excitation Wavelength							
x			0.64				
y			0.34				
CT [K]			1051				
$\Delta C$			0.003				
CRI			21.02				
For a 455nm Excitation Wavelength							
x	0.63	0.62	0.62				
y	0.34	0.34	0.34				
CT [K]	1063	1103	1103				
$\Delta C$	0.004	0.008	0.008				
CRI	25.58	27.21	31.62				

Color Property	Example 8	Example 9	Example 10	Example 11	Example 12
For a 370nm Excitation Wavelength					
x	0.37	0.37	0.39	0.39	0.39
y	0.39	0.39	0.41	0.41	0.40
CT [K]	4504	4486	4017	4015	4009



$\Delta C$	0.007	0.006	0.008	0.008	0.007
CRI	83.74	84.52	83.75	83.71	83.87
For a 380nm Excitation Wavelength					
x	0.44	0.45	0.44	0.44	0.44
y	0.43	0.43	0.40	0.40	0.40
CT [K]	3060	3050	2915	2913	2951
$\Delta C$	0.008	0.008	0.001	0.0007	0.0005
CRI	86.79	86.90	87.38	87.50	87.38

[0068] It will be noted that several of the examples achieve properties that may fall outside the scope of part of this invention. These examples thus demonstrate the importance of certain factors in achieving the properties of this invention and, most importantly, provide valuable guidance as to how routine experimentation may be utilized to select compositions within the general composition space defined for this invention and excitation conditions (wavelength and excitation bandwidth) which have resultant properties defined for this invention.

[0069] A white LED system of this invention can be constructed in a number of ways. Figure 9 is a schematic drawing of a white LED system prepared from a highly doped rare earth phosphate phosphor glass prepared in the form of a solid disk. In Figure 9, the glass component is placed between the EV or blue LED active element and the outside environment. The disk serves a double role as a hermetic barrier between the LED element and the ambient air and as a white light generation source in the white LED. The UV or blue emission from the LED

is absorbed by the highly rare earth doped glass and re-emitted as white light. Figure 10 is a schematic drawing of a white LED system prepared from a highly doped rare earth phosphate phosphor glass prepared in the form of a glass powder that is placed in a second suitable host matrix, placed adjacent to the UV or blue LED element, and jointly encapsulated by a epoxy, plastic, or other organic potting material common within the LED industry. As before, in Figure 10, the UV or blue emission from the LED is absorbed by the highly rare earth doped glass and re-emitted as white light. Similar devices can be prepared by other technologies, for example the glass composition can be prepared by sputtering processes or as a sol gel solution, or multiple UV and blue emitting LED can be placed adjacent to the high rare earth doped phosphate phosphor glass.

[0070] The entire disclosures of all applications, patents and publications, cited above or below, is hereby incorporated by reference.

[0071] From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention and, without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

What is claimed is: